

Microwave remediation of soil contaminated with hexachlorobenzene

Songhu Yuan, Meng Tian, Xiaohua Lu*

Environmental Science Research Institute, Huazhong University of Science and Technology, Wuhan 430074, PR China

Received 15 November 2005; received in revised form 3 March 2006; accepted 3 March 2006

Available online 8 August 2006

Abstract

This study describes the remediation of hexachlorobenzene (HCB) contaminated soils by microwave (MW) radiation in a sealed vial. When powdered MnO_2 was used as MW absorber, a complete removal of HCB was obtained with 10 min MW by the addition of H_2SO_4 (50%). But no significant decomposition was observed by the addition of NaOH (10 mol/L) or H_2O in the same conditions. In contrast, when powdered Fe was used instead of MnO_2 , the difference of HCB removals between H_2SO_4 and NaOH were not obvious. It is noteworthy that more than 95% removal was achieved in any case when the sole aqueous solution of H_2SO_4 , NaOH, H_2O or Na_2SO_4 was added without MnO_2 or Fe. As a result, it is possible that water itself contained in the damp soil may act as MW absorber and remediate the contaminated soil without addition of any other MW absorbers. Gas chromatograph/mass spectrum (GC/MS) analysis detected no intermediates in all the processes. The decomposition mechanism of HCB by MW radiation was suggested as the binding of HCB and soil. Whatever fragments formed from HCB by heat were tightly bound to the soil, making it impossible to extract them out. In the end, treatment of practical HCB contaminated soil by MW reduced HCB from 55.8 mg/kg to 0.91 mg/kg.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Microwave; Hexachlorobenzene; Soil remediation; Manganese dioxide; Iron

1. Introduction

Hexachlorobenzene (HCB) is a typical persistent organic pollutant. It is semi-volatile, mobile in the environment and bioaccumulation [1]. Despite the ban and restriction on the usage in developed countries during the 1970s and 1980s, some developing countries are still using HCB for agricultural and public purposes because of the low cost and versatility in controlling various insects [2]. HCB has been widely used as a fungicidal dressing of seed grains and is a waste byproduct in many industrial processes [3]. High concentration of HCB contaminated soil has been found by our group in the vicinity of Wuhan in central China [4]. Presently, the contamination of soil and sediment by HCB is still a very serious hazardous problem. Therefore, it is emergent to develop effective processes to remediate the contaminated site.

Microwaves (MW) are a separate band of electromagnetic radiation with frequencies in the range of 300 MHz to 300 GHz. According to their response in MW field, materials are classi-

fied into three groups, conductor, insulators and absorbers [5]. Materials that absorb MW radiation are called dielectrics. The interaction between dielectrics and microwave results in energy absorption. Generally, the dielectric properties of a material are related to temperature, moisture content, density and material geometry [5]. MW energy induces molecular motion by rotation of dipoles and migration of ions. The major advantages of MW heating are rapid, uniform and selective [6,7]. Apart from the application in organic synthesis [8], polymerization and dehydration processes [9,10], inorganic synthesis [11], safety and biological aspects [12], analyses and extraction [13] and food sterilization [14], MW technique has found its place in environmental engineering. A comprehensive review of MW in the field of environment was reported by Jones et al. [5]. In the remediation of contaminated soils, compared with other technologies such as vapor extraction, surfactants or solvent flushing, chemical oxidation, biological treatment and so on, MW can achieve a faster removal of pollutants whether the soils are permeable or not. Studies have been reported using MW radiation to remediate organic and heavy metal contaminated soils [15–22].

Abramovitch et al. [15] investigated the decomposition of HCB, pentachlorophenol (PCP), 2,2',5,5'-tetrachlorobiphenyl and 2,2',4,4',5,5'-hexachlorobiphenyl in soil using microwave

* Corresponding author. Tel.: +86 27 87792159; fax: +86 27 87792159.
E-mail address: lxh@hust-esri.com (X. Lu).

energy in a modified ceramic alumina bomb. The most efficient decomposition was achieved by the addition of powdered Cu_2O or Al and 10 mol/L NaOH. Minute amounts of decomposition products could be extractable from the soil after MW remediation. Vast majority of the decomposition products were supposed to be either mineralized or tightly bound to the soil. The authors further studied MW remediation of polluted soils in situ in an open vessel [16–18]. Graphite and metal rod were used instead of Cu_2O and Al powder because they can be pressed down to a preset depth to focus and transport MW energy [16].

MnO_2 is one of the strongest MW absorbers. It can be obtained easily and is environmentally friendly. MnO_2 has been used to shorten the organic synthetic time with MW [23], but there is no report using it as MW absorber to remediate contaminated soils. In addition, the water contained in damp soils is also a good MW absorber. It can absorb microwave energy and heat soils to high temperature. Due to the saving of the adding and mixing of MW absorbers, it is meaningful if the water contained in the damp soil can work well. Moreover, it is noteworthy that practical contaminated soils have never been treated with MW radiation.

In the present study, both simulated and practical HCB contaminated soils were treated with MW radiation. The objectives are: (1) to evaluate the viability of MW remediation of HCB contaminated soil using MnO_2 as MW absorber, (2) to investigate the effect of MW remediation using the water itself contained in the damp soil as MW absorber, (3) to provide further information about the MW remediation of organic polluted soils and (4) to treat practical HCB contaminated soil.

2. Materials and methods

2.1. Chemicals and materials

HCB (99.9%) was obtained from Shanghai General Factory of Reagent, Shanghai, China, and PCP (98.5%) from Qingpu Synthetical Reagent Factory, Shanghai, China. MnO_2 powder (analytical grade) was purchased from Tianjin Kermel Chemical Reagent Development Center, China, and Fe powder (analytical grade) was from Xiangzhong Geological Experimental Research Institute, China. Acetone (analytical grade) was used for the dissolution of HCB and hexane (analytical grade) for the extraction of HCB. Deionized water (18.2 m Ω cm) obtained from a Millipore Milli-Q system was used for the preparation of solutions. All the other reagents were above analytical grade.

Diatomite (chemical purity, Tianjin Kermel Chemical Reagent Development Center, China) was used as simulated soil. Two hundred grams dry diatomite was spiked with 10 mL HCB acetone solution (1000 mg/L) and 20 mL pure acetone. The simulated HCB contaminated soil was then dried in air for 24 h to evaporate acetone and stored in dark bottle for usage. The HCB concentration was determined as 52 mg/kg, which represents the typical concentration found in the vicinity of Wuhan city. The same process was used to prepare HCB contaminated kaolin (chemical purity, Guoyao Group Chemical Reagent Co., Ltd., China), which is a typical clayed soil.

Practical soil was sampled close to a chemical plant, which utilizes HCB and NaHS to produce $\text{C}_6\text{Cl}_5\text{SH}$. The soil sample was first dried at 105 °C for 5 h, then ground and sieved by 200 mesh screen. The sample was stored in dark bottle in refrigerator (4 °C) for treatment. The HCB concentration was determined as 55 mg/kg.

2.2. Procedures and equipment

0.5000 g HCB contaminated diatomite was placed in a 10 mL vial, then 0.0500 g MnO_2 or Fe powder was added and mixed thoroughly. In the end, 0.15 mL aqueous solution of H_2SO_4 , NaOH, H_2O or NaSO_4 was introduced and mixed. The vial was sealed with PTFE lid and radiated in a domestic microwave oven (750 W, 2.45 GHz) for a preset time. For the treatment of practical HCB contaminated soil, 5.000 g sample was used instead and the other procedures were the same. At least triplicate runs were repeated for all the cases.

2.3. Analysis of the samples

2.3.1. Sample pretreatment prior to analysis

2.3.1.1. Simulated soil sample. When the vial was cooled to room temperature, it was uncovered and 5.00 mL hexane was added. Then the vial was sealed immediately and mixed thoroughly. The extraction process was assisted by 30 min ultrasonication (20 kHz). After the sample was centrifuged for 3 min at 3000 rpm, the supernatant was poured out to another vial for gas chromatography (GC) and gas chromatography/mass spectrum (GC/MS) analysis.

2.3.1.2. Practical soil sample. When the vial was cooled to room temperature, the soil was poured out and dried in air for 24 h, ground and sieved by 200 mesh screen. 0.5000 g dried soil was taken and 5 mL hexane was added. The subsequent procedures were the same as those for simulated soil. Such a different pretreatment process was employed because the practical soil is clayed and the extraction in wet is not quantitative.

2.3.2. HCB analysis

An HP 6890 GC equipped with an electron capture detector (ECD) and an HP-1 column (30 m length, 0.32 mm i.d., 0.25 μm film thickness) was used to analyze HCB in the extract. The temperature program of the GC started at 150 °C and was held for 1 min. Then the column was sequentially heated at a rate of 20 °C/min to 200 °C, held for 10 min. The flow rate of carrier gas (nitrogen 99.999%) was 1.5 mL/min. The inlet and detector temperatures were 250 °C and 300 °C, respectively. One microlitre extract was injected with a split ratio of 10.

2.3.3. Intermediates identification

A Varian Saturn 2100T GC/MS was used to identify the intermediates produced in the processes and the materials contained in the practical soil. A Varian 3900 GC equipped with a FactorFour capillary column (30 m length, 0.25 mm i.d., 0.25 μm film thickness) was used. The temperature program of the GC started at 100 °C and was held for 2 min. Then the column was

Table 1
HCB recovery for different composition

Composition	HCB (mg/kg)	Recovery (%)
Diatomite (0.5000 g)	52.0	–
Diatomite (0.5000 g) + 0.15 mL NaOH (10N)	52.7	101
Diatomite (0.5000 g) + 0.0500 g MnO ₂	49.7	95.6
Diatomite (0.5000 g) + 0.15 mL H ₂ SO ₄ (50%) + 0.0500 g MnO ₂	38.8	74.6
Diatomite (0.5000 g) + 0.15 mL NaOH (10N) + 0.0500 g MnO ₂	51.0	98.1
Diatomite (0.5000 g) + 0.15 mL H ₂ O + 0.0500 g MnO ₂	37.7	72.5
Diatomite (0.5000 g) + 0.15 mL H ₂ SO ₄ (50%) + 0.0500 g Fe	46.3	89.0
Diatomite (0.5000 g) + 0.15 mL NaOH (10N) + 0.0500 g Fe	33.3	64.0
Practical soil (0.5000 g)	55.8	–
Practical soil (0.5000 g) + 0.15 mL H ₂ O	8.33	14.9
Kaolin (0.5000 g)	45.5	–
Kaolin (0.5000 g) + 0.15 mL H ₂ O	18.6	40.9
Kaolin (5.0000 g) + 1.5 mL H ₂ O ^a	36.5	80.2

^a The sample was dried by airing for 24 h. Then it was ground and sieved through 200 mesh screen. 0.5000 g kaolin was taken for pretreatment and analysis.

sequentially heated at a rate of 15 °C/min to 170 °C, held for 1 min, a rate of 5 °C/min to 200 °C, held for 5 min and a rate of 15 °C/min to 235 °C, held for 10 min. The flow rate of carrier gas (Helium, 99.995%) was 1.0 mL/min. The inlet temperature was 250 °C and the split ratio was 15. A Varian CP-8410 AutoInjector was equipped and the injection volume was 1 µL. The MS was equipped with an electron ionization (EI) source with a scan range from *m/z* 40 to *m/z* 400. The solvent delay was 3 min.

2.4. Quality control

All the glassware such as vials and bottles were first cleaned in an ultrasonic cleaner (20 KHz) assisted by liquor for 30 min. Then they were further washed by tap water and deionized water for three times, respectively. Organic solvents were newly purchased from manufacturers and are above analytical grade purity. Deionized water was obtained from a Millipore Milli-Q system (18.2 mΩ cm).

The uniform distribution of HCB in the simulated HCB contaminated diatomite, kaolin and practical HCB contaminated soil was verified by the consistency of GC analysis of three random samples. MW radiation was performed in triplicate to minimize the errors due to the uneven distribution of MW field. All the other experiments including recovery test and shaking table were repeated at least three times. In the GC analysis, a calibration curve ($R^2 > 0.996$) included more than four points was made to measure the HCB concentration. Each sample was injected twice to ensure a good reproducibility. Sample blanks were regularly injected to ensure that the system was not contaminated. The syringe was rinsed with solvent several times between sample injections to avoid cross-contamination.

3. Results and discussion

3.1. Recovery test

It is difficult to achieve a good recovery of HCB in soils, particularly in clayed soils. So a series of primary tests were carried out to examine the recovery in different soil samples. The results are listed in Table 1.

Table 1 shows that the recovery of HCB in diatomite was mostly over 70% with the adding of aqueous solution and MnO₂ (or Fe). Diatomite is permeable and easy to be dispersed, so HCB can be quantitatively extracted. While in the practical soil and kaolin, the recoveries were 14.9% and 40.9%, respectively. The practical soil and kaolin are clayed and will agglomerate in the presence of aqueous solution. It was found that both soils could not be dispersed in the extraction process even assisted by ultrasonication. After the evaporation of water in air, a good dispersion was observed. The recovery of HCB in kaolin could achieve 80.2%. So, the pretreatment process of airing is viable for the quantitative analysis of clayed soil.

3.2. Decomposition of HCB in the presence of MnO₂

As a strong oxidant and MW absorber, MnO₂ has been used to shorten the reaction period of organic synthesis with MW [23]. However, MnO₂ has never been used for the remediation of polluted soil under MW radiation. In order to simulate moisture, aqueous solutions of H₂SO₄, NaOH or H₂O were added quantitatively. The removals of HCB by the addition of MnO₂ and different aqueous solutions are plotted in Fig. 1.

In Fig. 1, the removals at 0 min were resulted from the recovery of HCB in the pretreatment process, as discussed in Section

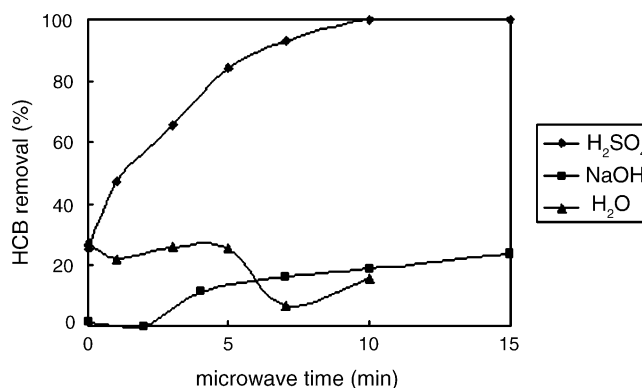


Fig. 1. Removal of HCB in MW by the addition of MnO₂ and different aqueous solutions. [H₂SO₄] = 50%, [NaOH] = 10 mol/L.

Table 2
Comparative results

Processes	Removal (%)
Diatomite + MW 10 min	6.2
Diatomite + 0.0500 g MnO ₂ + MW 10 min	40.4
Diatomite + 0.15 mL H ₂ SO ₄ (50%) + MW 10 min	95.6
Diatomite + 0.15 mL H ₂ O + MW 10 min	93.3
Diatomite + 0.15 mL NaOH (10N) + MW 10 min	92.5
Diatomite + 0.0500 g MnO ₂ ^a	7.5
Diatomite + 0.0500 g MnO ₂ + 0.15 mL H ₂ SO ₄ (50%) ^a	35.0
Diatomite + 0.0500 g MnO ₂ + 0.15 mL H ₂ O ^a	32.7
Diatomite + 0.0500 g MnO ₂ + 0.15 mL NaOH (10N) ^a	22.3

^a The samples were shaken in a shaker at 25 °C for 24 h.

3.1. It can be seen that the decomposition of HCB was fast and no residue was detected with 10 min MW in H₂SO₄ media. When NaOH or H₂O was used, no significant removal was observed. In order to explore the effect of MnO₂ on the removal of HCB, the comparative experiments were conducted and the results are given in Table 2. Both HCB and SiO₂ contained in the dry diatomite cannot absorb MW energy, so negligible removal was observed when the soil was radiated with MW alone. With the addition of MnO₂, the removal of 40.4% was achieved with 10 min MW. It can be inferred that MnO₂ can decompose HCB singly. Theoretically, if the chemical structure of MnO₂ does not change, the temperature will increase sharply to above 1000 °C. Such a high temperature will lead to the vitrification of soils and an almost complete removal of HCB [15,24]. Here only 40.4% removal suggests the change of the chemical structure of MnO₂. It was reported that MnO₂ would be transformed to Mn₃O₄ by thermal decomposition at high temperature in the range of 1000–1100 °C [24]. Seven minutes are enough to heat MnO₂ to above 1000 °C in microwave oven (650 W, 2.45 GHz) [24]. Because Mn₃O₄ is transparent to MW and the transformation of Mn₃O₄ from MnO₂ absorbs great heat ($\Delta H_{298}^{\circ} = +174.3$ kJ/mol) [24], the temperature will decrease after 7 min. As a result, the formation of Mn₃O₄ may be accounted for the low removal of HCB.

However, it is surprising that more than 92% removal of HCB was achieved by the addition of aqueous solutions of H₂SO₄, NaOH or H₂O alone with 10 min MW. H₂O is also a typical polar substance that can greatly absorb MW energy [25]. Therefore, it can be inferred that high temperature and pressure appear in the vial. These conditions may lead to many complex reactions. One possible reaction is the thermal decomposition of HCB, which produces small molecule fragments. The fragments are possibly bound to soils tightly, or form unimolecular layers and retain indefinitely [16]. As the temperature increases, some of the substances are entrapped in the interlamellar regions of the clay before desorption [16]. It is also possible that some chemical binding occurred between the oxygenated and chlorinated molecules and Al³⁺ octahedral at the clay edges [26]. All the possibilities contribute to the high removals of HCB in the presence of aqueous solution.

It can be concluded that MnO₂ only contributes to HCB decomposition in strong acidic media and restricts the decomposition in basic and neutral media. This result has never been

Table 3
Effect of acidity on the decomposition of HCB

Processes	Removal (%)
Diatomite + MnO ₂ + aqueous (50% H ₂ SO ₄) + MW 10 min	100
Diatomite + MnO ₂ + aqueous (40% H ₂ SO ₄) + MW 10 min	95.8
Diatomite + MnO ₂ + aqueous (30% H ₂ SO ₄) + MW 10 min	84.2
Diatomite + MnO ₂ + aqueous (20% H ₂ SO ₄) + MW 10 min	79.5
Diatomite + MnO ₂ + aqueous (10% H ₂ SO ₄) + MW 10 min	68.9
Diatomite + MnO ₂ + aqueous (5% H ₂ SO ₄) + MW 10 min	22.8
Diatomite + MnO ₂ + aqueous (pH 1) + MW 10 min	No removal
Diatomite + MnO ₂ + aqueous (pH 7) + MW 10 min	No removal
Diatomite + MnO ₂ + aqueous (pH 11) + MW 10 min	No removal
Diatomite + MnO ₂ + aqueous (10N NaOH) + MW 10 min	No removal

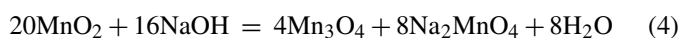
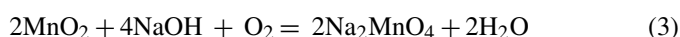
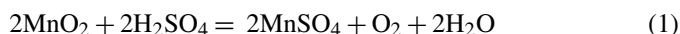
The dosage of diatomite, MnO₂ and aqueous solutions were 0.5000 g, 0.0500 g and 0.15 mL, respectively.

reported. The shaking table experiments in normal conditions show that the decomposition of HCB at 25 °C was minimal by the addition of any of the three aqueous solutions. It can be concluded that the decomposition of HCB by MnO₂ at normal temperature is very difficult whether in acidic, neutral or basic condition.

It has been found that MnO₂ restricted the decomposition of HCB in basic and neutral media, so the effect of acidity was investigated. Table 3 shows that stronger acidity led to larger decomposition. Manganese has valency such as +2, +3, +4, +6 and +7. Manganese with different valency can be transformed in specific conditions. With MW radiation, both aqueous solution and MnO₂ absorb MW energy, but MnO₂ predominates. Therefore, MW energy is focused on MnO₂ regardless of the existence of aqueous solution. Three possible processes happen for MnO₂ in acidic condition with MW radiation. One is the absorption of MW energy by MnO₂ and the subsequent energy transportation to surroundings and reactions (reactions (1) and (2); termed P1), one is the formation of MnSO₄ in strong acidic condition (reaction (1); termed P2) and the other is the transformation of MnO₂ to Mn₃O₄ (reaction (2); termed P3). P1 may happen in any conditions. The energy transported to the surroundings contributes to the decomposition of HCB, while the energy transported to the reactions such as reaction (2) restricts the decomposition due to the waste of energy. The effect with 50% H₂SO₄ can be explained as the strong absorption of MW energy and its quick transportation to the surroundings. This will result in high temperature and pressure in the vial. P2 needs concentrated acid (H₂SO₄) [27]. When the electrolyte of MnSO₄ is produced from MnO₂, the absorption of MW energy by the mixture drops remarkably. P3 requires high temperature (1000–1100 °C) [24]. Mn₃O₄ is transparent to MW radiation. The energy for P3 is solely obtained from P1. Due to the great waste of energy ($\Delta H_{298}^{\circ} = +174.3$ kJ/mol), P3 restricts the decomposition of HCB.

It was observed that PTFE lid melt occasionally only when the acidity was more than 50%. The result suggests that H₂SO₄ with concentration larger than 50% leads to higher temperature than that with low concentration. Moreover, the light pink materials only appeared with the acidity more than 30%. It can be inferred that reaction (1) happens because most of the hydrates

of manganese sulfate are pink [27]. With the decrease of acidity, reaction (1) was increasingly restricted. MnO_2 predominately absorbed MW energy and heated itself to high temperature, leading to the formation of Mn_3O_4 . Thus the decomposition of HCB reduced correspondingly. On the other hand, reaction (3) is possible in basic condition (10N NaOH). Mole of MnO_2 was calculated as $50/97 = 0.52$ mmol, O_2 as $10 \times 0.21/22.4 = 0.09$ mmol and NaOH as $0.15 \times 10 = 1.5$ mmol (10 is the volume of the vial, 0.21 is the content of O_2 in air, 22.4 is the mole volume of gas at standard condition and 0.15 is the volume of NaOH solution). Reaction (3) happened slightly because of the shortage of O_2 . However, reaction (2) generates O_2 through the thermal decomposition of MnO_2 . Reaction (4) was obtained by combining reactions (2) and (3). Mn_3O_4 and Na_2MnO_4 were the final products in strong basic condition by MW radiation. Mn_3O_4 and Na_2MnO_4 are almost transparent to MW, furthermore, they impede the transportation of energy from the MW absorbers to the surroundings. Consequently, the restriction in neutral and basic conditions was observed. The results are different from the literatures using Cu_2O , Al, Zn and so on [15,16].



In order to explore the fate of HCB with MW radiation, GC/MS analysis was performed. However, no new materials were detected. Negligible quantity of intermediates were likely produced, however, they were not detected owing to the sensitivity of GC/MS. This is in good agreement with Abramovitch's study [15], where powdered Al or Cu_2O and 10N NaOH were used to decompose HCB with MW radiation. The author further used ^{14}C -labelled PCB as target [16], but less than 2.5% mineralization was measured when 78% decomposition was achieved. The mechanism of HCB decomposition in this study is similar to that suggested by Abramovitch et al. [15]. HCB was probably thermally decomposed to fragments, which were further tightly bound to the soil or form unimolecular layers and retained indefinitely [16]. It was also possible that some chemical binding occurred between the oxygenated and chlorinated molecules and Al^{3+} octahedral at the clay edges [26].

In summary, the mechanism of the decomposition of HCB using MnO_2 as MW absorber is very complex because the many chemical reactions happen in MW radiation. The viability is primarily denied by the harsh conditions required (>50% H_2SO_4). Till now, the value of this section can be considered to provide insight information on the behavior of MnO_2 in MW radiation and to afford guidance for the selection of MW absorbers.

3.3. Decomposition of HCB in the presence of Fe

In order to get comparative results to MnO_2 , powdered Fe, a strong reductant and microwave conductor, was used in the decomposition of HCB with MW. The results are shown in Fig. 2.

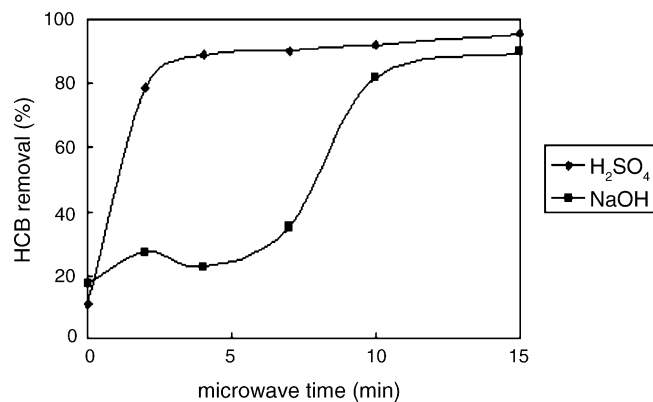


Fig. 2. Removal of HCB in MW by the addition of Fe and different aqueous solutions. $[\text{H}_2\text{SO}_4] = 50\%$, $[\text{NaOH}] = 10$ mol/L.

Fig. 2 shows that the removal of HCB achieved 89.2% in 50% H_2SO_4 media with 4 min MW and attained 95.7% with 15 min MW by the addition of Fe, while 81.9% removal was achieved in 10N NaOH media when the radiation time reached 10 min. It was obvious that the decomposition of HCB was much faster in acidic media than in basic media. Similarly, the comparative experiments were performed to investigate the reaction mechanism. The results are displayed in Table 4. It can be seen that Fe alone had little effect on the decomposition of HCB with 10 min MW. However, the removals of 92.3% and 93.9% were obtained in H_2O and Na_2SO_4 media, respectively. Compared with the decomposition of HCB under MW radiation with different aqueous solutions (Table 2), it can be inferred that Fe restricts the decomposition of HCB in the first stage in basic media and has negligible enhancement in acidic and neutral media, whether H_2SO_4 , H_2O or Na_2SO_4 (Table 4).

In 50% H_2SO_4 ($0.15 \times 9.2 = 1.38$ mmol), Fe (50/56 = 0.89 mmol) was dissolved to FeSO_4 (reaction (5)), which shows similar MW response to MnSO_4 . Meanwhile, powdered Fe absorbed MW energy and transported the energy to the surroundings to decompose HCB. Therefore, the decomposition of HCB in acidic media was similar to that in aqueous solution. When 10N NaOH was used, the possible reaction was the combustion of Fe in MW radiation (reaction (6)). Fe_3O_4 absorbs MW energy more greatly than Fe. As a result, the decomposition of HCB increased greatly in the later stage.



Table 4
Comparative results in the presence of Fe

Processes	HCB (mg/kg)	Removal (%)
Diatomite	52.0	0
Diatomite + 0.0500 g Fe + MW 10 min	46.3	11.0
Diatomite + 0.0500 g Fe + 0.15 mL H_2O + MW 10 min	4.03	92.3
Diatomite + 0.0500 g Fe + 0.15 mL Na_2SO_4 (5.0 M) + MW 10 min	3.19	93.9

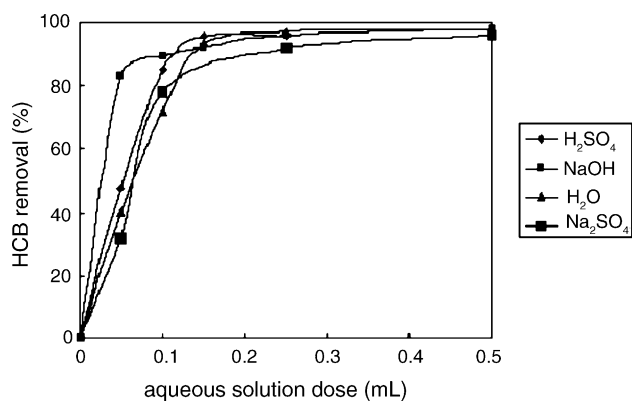


Fig. 3. Effect of aqueous solutions alone on the decomposition of HCB with 10 min microwave radiation. $[\text{H}_2\text{SO}_4] = 50\%$, $[\text{NaOH}] = 10 \text{ mol/L}$, $[\text{Na}_2\text{SO}_4] = 5 \text{ mol/L}$.

Similarly, no new intermediates were detected by GC/MS analysis in all the processes with powdered Fe. The result was similar to the literature [17], in which iron wire was used as MW conductor to decompose PAHs. A similar mechanism to that with MnO_2 was proposed for the decomposition of HCB with Fe.

3.4. Decomposition of HCB with aqueous solution alone

As shown in Table 2, all the four aqueous solutions alone had significant effect on the decomposition of HCB. This result is very meaningful because it provides a new alternative approach to clean contaminated soil by MW radiation without addition of any MW absorbers. So, additional experiments were conducted to investigate the effect with the addition of aqueous solution alone. The results are given in Fig. 3.

It can be seen from Fig. 3 that aqueous solutions alone could greatly decompose HCB with 10 min MW. This result has never been reported in literature. By the addition of 0.05 mL aqueous solutions, the sequence of HCB decomposition was: NaOH (83.2%) > H_2SO_4 (47.5%) > H_2O (39.8%) > Na_2SO_4 (31.9%). HCB is unstable in basic condition at high temperature, so a larger decomposition of HCB in NaOH media was observed. With the increase of the dosage of the aqueous solution, the difference of decomposition became negligible. Water contained in the damp soils increased sharply with the increase of dosage, which might be responsible for the negligible difference. In addition, no new intermediates were detected by GC/MS analysis. The mechanism has been discussed in Section 3.2.

With the rapid development of microwave technology, microwave power can achieve as high as hundreds of kilowatt, and the waveguide used to introduce microwave can be designed flexibly. Therefore, it is inspiring to provide the target plenty of heat in quite a short time. The application of microwave technology for soil remediation becomes more and more practical. Nevertheless, destroying the soils treated to some extent, MW technology can only be considered to be suitable for the remediation of soils where no plants will grow or which will be used as building materials.

3.5. Remediation of practical HCB contaminated soil

Three different processes were carried out in the remediation of practical HCB contaminated soil. Fig. 4 shows the changes of GC spectrums in these processes.

In the GC spectrums, the peak at 4.020 min was HCB. Combined with GC/MS analysis, the peak at 2.957 min was identified

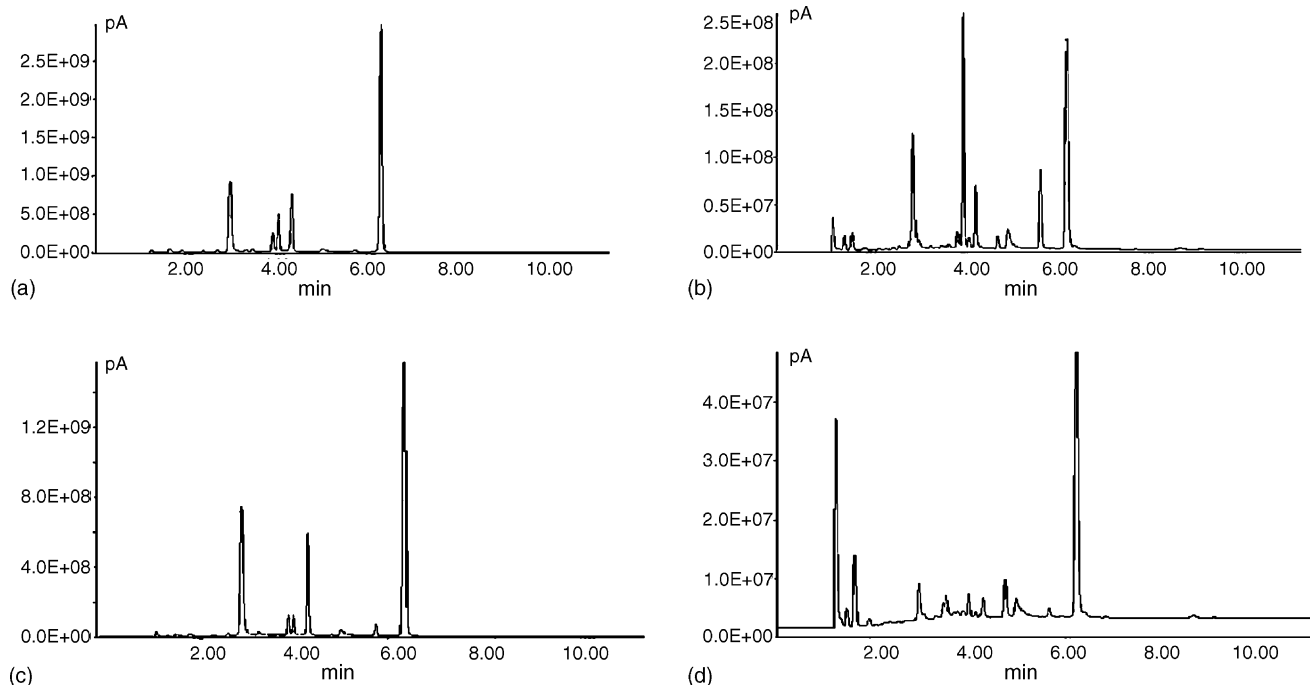


Fig. 4. GC spectrum changes. (a) original soil, (b) radiated with MW, (c) radiated with MW + H_2O , (d) radiated MW + NaOH.

Table 5
Removals of the main substances in three processes

Substances	Removal (%)		
	MW	MW + H ₂ O	MW + NaOH
HCB	60.2	71.3	98.4
S ₆	88.8	36.7	99.2
C ₆ Cl ₅ SH	91.2	44.5	98.6
S ₈	92.1	46.9	98.1

Where microwave time was 10 min, dosage of H₂O and NaOH (10N) was 1.50 mL, practical soil was 5.000 g. Initial concentration of HCB in the practical soil was determined as 55.8 mg/kg. Removals of the other substances were calculated by the variance of the corresponding peak area.

as cyclic hexatomic sulfur (S₆), 4.313 min was pentachlorothioarisoole (C₆Cl₅SH) and 6.275 min was cyclic octatomic sulfur (S₈). All these substances are the contents of the effluent from the chemical plant.

Table 5 displays the removals of the main substances in the three processes. The presence of S₆ and S₈ was the reason that resulted in the decomposition of all the substances in dry. The addition of H₂O restricted the decomposition of all the substances except HCB. NaOH greatly enhanced the decomposition of all the substances. This result may be probably because of the complicated composition of the practical soil, which possesses great amount of organic content, many mineral materials and ions. The removal of HCB with NaOH in MW was 98.4% and the residue HCB was detected as 0.91 mg/kg. So, it could be considered as an alternative approach to remediate the practical soil. Much work still needs to be done to investigate the engineering of the method.

4. Conclusions

A fundamental research was carried out to explore the microwave remediation of HCB contaminated soil. Conclusions are drawn as follows.

- (1) The mechanism of the decomposition of HCB using MnO₂ as MW absorber is very complex because many chemical reactions were involved under MW radiation. The viability was primarily denied by the harsh conditions required ($\geq 50\%$ H₂SO₄). However, this study provided insight information on the behavior of MnO₂ in MW radiation and offered guidance for the selection of MW absorbers. In contrast, powdered Fe restricted the decomposition of HCB in the first stage in basic media and had slight enhancement on the decomposition in acidic and neutral media. The mechanism of the decomposition of HCB with Fe was proposed to be similar to that with MnO₂.
- (2) The aqueous solution alone shows an excellent effect on the decomposition of HCB with 10 min MW radiation. The decomposition increased with the increase of the aqueous dosage. The result provided an alternative approach for the remediation of contaminated soil with MW.
- (3) HCB was probably thermally decomposed to fragments, which were further tightly bound to the soil or form uni-

molecular layers and retained indefinitely. It was also possible that some chemical binding occurred between the oxygenated and chlorinated molecules and Al³⁺ octahedral at the clay edges.

- (4) Microwave radiation can be considered as an alternative approach for the remediation of practical HCB contaminated soil. HCB and other pollutants in the practical soil could be decomposed greatly in the basic media particularly. The removal of HCB with NaOH in MW was 98.4% and the residue HCB was detected as 0.91 mg/kg.

Acknowledgements

This work was supported by the key project of Ministry of Education of China (No. 104250) and the key project of Natural Science Foundation of Hubei Province.

References

- [1] H.R. Pohl, P.R. McClure, M. Fay, J. Holler, C.T. Rosa, Public health assessment of hexachlorobenzene, *Chemosphere* 43 (2001) 903–908.
- [2] R.E. Bailey, Global hexachlorobenzene emissions, *Chemosphere* 43 (2001) 167–182.
- [3] F. Brahusi, U. Dcorer, R. Schroll, J.C. Munch, Stimulation of reductive dechlorination of hexachlorobenzene in soil by inducing the native microbial activity, *Chemosphere* 55 (2004) 1477–1484.
- [4] Q.J. Xie, T. Ma, L.L. Wang, X.H. Lu, Primary study of the treatment of hexachlorobenzene contaminated sediments by electro-Fenton method, *J. Huazhong Univ. Sci. Technol. (Nat. Sci. ed., CHN)* 33 (2005) 122–124.
- [5] D.A. Jones, T.P. Lelyveld, S.D. Mavrofidis, S.W. Kingman, N.J. Miles, Microwave heating applications in environmental engineering—a review, *Resour. Conserv. Recy.* 34 (2002) 75–90.
- [6] G.N. Mavrogianopoulos, A. Frangoudakis, J. Pandelakis, Energy efficient soil disinfestation by microwaves, *J. Agric. Eng. Res.* 75 (2000) 149–153.
- [7] C.H.G. Jou, H.S. Tai, Application of granulated activated carbon packed-bed reactor in microwave radiation field to treat BTX, *Chemosphere* 37 (1998) 685–698.
- [8] L. Mats, H. Anders, Microwave-assisted high-speed chemistry: a new technique in drug discovery, *Drug Discov. Today* 6 (2001) 406–416.
- [9] R. Correa, G. Gonzalez, V. Dougar, Emulsion polymerization in a microwave reactor, *Polymer* 39 (1998) 1471–1474.
- [10] T. Funebo, T. Ohlsson, Microwave-assisted air dehydration of apple and mushroom, *J. Food Eng.* 38 (1998) 353–367.
- [11] Y. Fang, A.O. Hu, J.O.J. Shixi, The effect of calcinations on the microwave dielectric properties of Ba(Mg_{1/3}Ta_{2/3})O₃, *J. Eur. Ceram. Soc.* 21 (2001) 2745–2750.
- [12] S. Banik, S. Bandyopadhyay, S. Ganguly, Bioeffects of microwave—a brief review, *Bioresour. Technol.* 87 (2003) 155–1559.
- [13] M. Ericsson, A. Colmsjo, Dynamic microwave-assisted extraction, *J. Chromatogr. A* 877 (2000) 141–151.
- [14] T.T. Chau, K.C. Kao, G. Blank, F. Madrid, Microwave plasmas for low-temperature dry sterilization, *Biomaterials* 17 (1996) 1273–1277.
- [15] R.A. Abramovitch, B.Z. Huang, M. Davis, et al., Decomposition of PCB's and other polychlorinated aromatics in soil using microwave energy, *Chemosphere* 37 (1998) 1427–1436.
- [16] R.A. Abramovitch, B.Z. Huang, D.A. Abramovitch, et al., In situ decomposition of PCBs in soil using microwave energy, *Chemosphere* 38 (1999) 2227–2236.
- [17] R.A. Abramovitch, B.Z. Huang, D.A. Abramovitch, et al., In situ decomposition of PAHs in soil and desorption of organic solvents using microwave energy, *Chemosphere* 39 (1999) 81–87.
- [18] R.A. Abramovitch, M. Capracotta, Remediation of waters contaminated with pentachlorophenol, *Chemosphere* 50 (2003) 955–957.

- [19] R.A. Abramovitch, C.Q. Lu, E. Hicks, et al., In situ remediation of soils contaminated with toxic metal ions using microwave energy, *Chemosphere* 53 (2003) 1077–1085.
- [20] H.S. Tai, C.J.G. Jou, Immobilization of chromium-contaminated soil by means of microwave energy, *J. Hazard. Mater.* 65 (1999) 267–275.
- [21] Q. Gan, A case study of microwave processing of metal hydroxide sediment sludge from printed circuit board manufacturing wash water, *Waste Manage.* 20 (2000) 695–701.
- [22] L.P. Carlos, A.C. Howard, Microwave induced pyrolysis of plastic wastes, *Ind. Eng. Chem. Res.* 40 (2001) 4749–4756.
- [23] R.S. Varma, R.K. Saini, E. Dahiya, Active manganese dioxide on silica: oxidation of alcohols under solvent-free conditions using microwaves, *Tetrahedron Lett.* 38 (1997) 7823–7824.
- [24] Q.H. Jin, *Microwave Chemistry*, Science Press, Beijing, China, 1999.
- [25] Z. Kawala, T. Atamanczuk, Microwave-enhanced thermal decontamination of soil, *Environ. Sci. Technol.* 32 (1998) 2602–2607.
- [26] J.D. Kubicki, M.J. Droh, L.M. Schroeter, S.E. Apitz, Bonding mechanisms of salicylic acid adsorbed onto illite clay: an ATR-FTIR and molecular orbital study, *Environ. Sci. Technol.* 31 (1997) 1151.
- [27] Q.Z. Meng, D.W. Hu, Q.S. Cheng, F.R. Kong, *Inorganic Chemistry*, Beijing Normal University Press, Beijing, China, 1988.